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(51) International Patent Classification ⁷ : C08K 5/51, C08L 55/02 // (C08K 5/51, 5:5333, 5:521)	A1	(11) International Publication Number: WO 00/17268 (43) International Publication Date: 30 March 2000 (30.03.00)
(21) International Application Number: PCT/US99/20847 (22) International Filing Date: 10 September 1999 (10.09.99) (30) Priority Data: 09/157,182 18 September 1998 (18.09.98) US 09/157,291 18 September 1998 (18.09.98) US (71) Applicant: ALBEMARLE CORPORATION [US/US]; 451 Florida Street, Baton Rouge, LA 70801-1765 (US). (72) Inventors: KUMAR, Govindarajulu; 5424 Foxridge Drive, Baton Rouge, LA 70817 (US). WORKU, Anteneh, Z.; 12074 Newcastle Avenue #1212, Baton Rouge, LA 70816 (US). (74) Agents: PIPPENGER, Philip, M. et al.; Albemarle Corporation, Patent and Trademark Division, 451 Florida Street, Baton Rouge, LA 70801-1765 (US).		(81) Designated States: CA, IL, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: HALOGEN-FREE FLAME RETARDANT THERMOPLASTIC POLYMER COMPOSITIONS (57) Abstract <p>Halogen-free flame retardant polymer compositions are made from an ABS resin as the sole resin, and a P, P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less as the sole phosphorus-containing flame retardant, or form at least one thermoplastic polymer and a combination of at least one of the foregoing P, P'-dihydrocarbyl pentaerythrityl diphosphonates, and at least one arylbis (dihydrocarbylphosphate) and/or at least one arylbis (dihydrocarbylphosphinate). Effective flame retardancy (UL-94 V-0) is achieved without material disruption of physical property requirements of the substrate polymer.</p>		

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HALOGEN-FREE FLAME RETARDANT THERMOPLASTIC POLYMER COMPOSITIONS

BACKGROUND

Heretofore certain pentaerythrityl diphosphonates have been proposed for use in the formulation of certain polymer compositions. Thus, in U.S. Pat. No. 3,141,032, C₁₋₁₈ dialkyl pentaerythrityl diphosphonates were proposed as flame retardants for polyolefins and cellulose acetate. German Offen. 26 30 693 proposed the use of a larger group of such diphosphonates as flame retardants for polyesters.

It was subsequently found, however, that despite these early proposals, various pentaerythrityl diphosphonates were ineffective as flame retardants in a variety of polymeric materials. Thus:

- U.S. Pat. No. 4,154,721 states that a di-C₁₋₈ alkyl or a di-C₆₋₂₀ aryl pentaerythrityl diphosphonate "alone is ineffective to impart any significant flame-retardant properties to the polymer composition . . ." According to this patent, the use of a halogenated organic compound containing at least about 30% of halogen in combination with the pentaerythrityl diphosphonate would give suitable flame retardancy to the polymeric substrate. It is taught in the patent that the pentaerythrityl diphosphonate behaves as a synergist, being ineffective in its own right, but serving to greatly enhance the flame retarding properties of the halogenated organic compound with which it is used.
- U.S. Pat. No. 4,162,278 teaches that di-C₈₋₁₈ alkyl pentaerythrityl diphosphonates "are not effective for flame retarding polyphenylene ether resins," and shows in Example 3 that when used individually at the level of 8% by weight in rubber-modified high impact polystyrene, seven different pentaerythrityl diphosphonates including dimethyl pentaerythrityl diphosphonate, diphenyl pentaerythrityl diphosphonate, and dibenzyl pentaerythrityl diphosphonate failed to pass the flammability test. The patent reports that di-substituted pentaerythrityl diphosphonate was effective for flame retarding blends of polyphenylene ether resins with rubber-modified high impact polystyrene only when the two substituents were methyl, phenyl, benzyl, or mono-, di- or trimethylbenzyl groups.
- U.S. Pat. No. 4,174,343 states that "[t]he diphosphonates have not been found to be useful by themselves in polyolefins to provide self-extinguishing nondripping polyolefin compositions." In fact, the patent shows in Examples 16-18 that each of dimethyl

pentaerythrityl diphosphonate, diphenyl pentaerythrityl diphosphonate, and dibenzyl pentaerythrityl diphosphonate when used alone at 30% by weight concentration in polypropylene failed the UL 94 vertical flame retardancy test. To achieve suitable flame retardancy in polyolefins, the patent resorts to use of a combination of a pentaerythrityl diphosphonate (each substituent on the phosphorus atoms being methyl, phenyl, benzyl or cyano group) and ammonium polyphosphate.

- U.S. Pat. No. 4,178,281 shows that 4% of dimethyl pentaerythrityl diphosphonate in polycarbonate gave a V-0 UL-94 rating. But in 50-50 blend of polycarbonate and ABS resin, 10% of dimethyl pentaerythrityl diphosphonate failed to meet the flame retardancy requirements of the UL-94 test. Dimethyl pentaerythrityl diphosphonate and diphenyl pentaerythrityl diphosphonate at the level of 20% gave V-0 and V-2 UL-94 ratings in a 50-50 blend of polycarbonate and an ABS resin. However, to flame retard blends of polycarbonate resin and ABS resin the patent states that "In most of these instances, however, it is desirable to use these phosphonates in combination with halogenated organic compounds wherein the halogen content is at least about 30%." And in discussing proportions of the components used, it is stated that "When the use of a halogenated organic compound is indicated, as, for example, in the case of alloys of polycarbonates and ABS resins, up to 30% may be used. Generally, it is unnecessary to use more than 20% of a halogenated organic compound, in combination with the phosphonate or phosphate, to achieve satisfactory flame retardant properties."
- U.S. Pat. No. 4,257,931 states: "The diphosphonates have not been found to be useful by themselves in flame retarding poly(1,4-butylene terephthalate) to provide self-extinguishing, non-dripping compositions." To impart effect flame retardancy properties to poly(1,4-butylene terephthalate), a combination is used composed of melamine pyrophosphate and a di-substituted pentaerythrityl diphosphonate where the substituents are cyano, methyl, phenyl, benzyl, or benzyl having 1-4 methyl groups on the ring.

Because of environmental concerns attributed to halogen-containing additives often used in polymeric materials, considerable efforts have been expended in the search for effective flame retardant additives that are free of halogen. Similar concerns exist about antimony-containing additive components in polymeric materials.

Apart from the question of effectiveness against flammability, another concern is the need to achieve effective flame retardancy of an ABS substrate polymer without significant reduction in its heat distortion temperature properties. Because of their inherent plasticizing properties,

many known phosphorus flame retardants cause significant reductions in heat distortion temperature of ABS as evidenced by low VICAT temperatures. Thus, a need exists for an effective way of flame retarding ABS polymers without significantly reducing its heat distortion temperature.

BRIEF SUMMARY OF THE INVENTION

Pursuant to one aspect of this invention it has been found that, in the case of ABS resins, it is possible to achieve very effective flame retardancy without materially reducing the heat distortion temperature of the polymer as reflected by VICAT temperatures. These advantageous results are made possible by use of a particular dihydrocarbyl-substituted pentaerythrityl diphosphonate without use of organic halogen-containing additives or other phosphorus-containing flame retardant additives or synergists such as ammonium polyphosphate or melamine pyrophosphate. Thus this aspect of the invention meets the strong desire, or even need, in the art for flame retardancy without use of organic halogen-containing materials, while at the same time providing a composition which can contain a single phosphorus additive component to achieve excellent flame retardant properties. Indeed, this aspect of the invention makes it possible to provide highly economical ABS resin compositions that are entirely free of the environmental concerns attributed to halogen-containing additives and antimony-containing components often used in polymeric materials. In addition, this aspect of the invention makes it possible to provide flame retarded ABS compositions in which the physical properties needed for end use applications are not materially impaired.

Accordingly, this aspect of the invention provides in one of its embodiments a halogen-free flame retardant polymer composition which comprises a blend made from (a) an ABS resin, and (b) a flame retardant amount of at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less; with the provisos that (c) the ABS resin is the sole polymeric component of the composition, (d) the P,P'-dihydrocarbyl pentaerythrityl diphosphonate is, or the P,P'-dihydrocarbyl pentaerythrityl diphosphonates are, the sole phosphorus-containing flame retardant component(s) of the composition, and (e) the composition is devoid of any phosphorus-containing flame retardant synergist and any antimony-containing flame retardant synergist.

A second aspect of this invention involves the discovery, *inter alia*, that by using one or more of the above P,P'-dihydrocarbyl pentaerythrityl diphosphonates together with certain diphosphates or diphosphinates it is possible to achieve excellent flame retardancy, while at the same time achieving an excellent balance between high heat distortion temperatures as reflected

by VICAT temperatures and high impact strength as reflected by Izod impact strength values. In fact, use of appropriate amounts and relative proportions of the diphosphate or diphosphinate together with the P,P'-dihydrocarbyl pentaerythrityl diphosphonate, makes possible further improvements in the overall physical properties of the resultant flame retarded polymer composition without sacrifice of the flammability resistance of the composition.

Moreover, these advantageous results of the second aspect of this invention are made possible in a variety of thermoplastic polymers by use of these phosphorus additive combinations without use of any halogen-containing additive components. Thus this aspect of the invention meets the strong desire, or in some cases even the need, in the art for flame retardancy without use at least of organic halogen-containing materials, while at the same time providing a composition which can achieve excellent flame retardant properties without material sacrifice of physical properties. Indeed, this aspect of the invention makes it possible to provide highly economical thermoplastic compositions that are entirely free of the environmental concerns attributed to halogen-containing additives and also antimony-containing components often used in polymeric materials. In addition, this aspect of the invention makes it possible to provide flame retarded thermoplastic compositions in which the physical properties needed for end use applications are not materially impaired.

Accordingly, this aspect of the invention provides in one of its embodiments a halogen-free flame retardant additive composition which comprises a blend made from (a) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less, and (b) at least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) in an (a):(b) weight ratio in the range of 1:1 to 20:1, and preferably in the range of 4:1 to 6:1. Preferably, the additive composition is also antimony-free.

In yet another embodiment of this aspect of the invention there is provided a halogen-free flame retardant polymer composition which comprises a blend made from (i) at least one thermoplastic polymer, and a flame retardant amount of (ii) a combination of (a) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less, and (b) at least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) in an (a):(b) weight ratio in the range of 1:1 to about 20:1, and preferably in the range of 4:1 to 6:1. Preferably, the polymer composition is also antimony-free.

In connection with polymer blends of any of the above embodiments of this invention that can be molded or extruded (*i.e.*, expressed through a die) without further dilution with substrate polymer, the term "flame retardant amount" as used herein, including the claims hereof, means that (1) the amount of the P,P'-dihydrocarbyl pentaerythrityl diphosphonate(s) when used as the sole phosphorus-containing flame retardant component(s) pursuant to the above first aspect, and (2) the total amount of the combination of P,P'-dihydrocarbyl pentaerythrityl diphosphonate(s) and arylbis(dihydrocarbylphosphate(s)) and/or arylbis(dihydrocarbylphosphinate(s)) used as the combined phosphorus-containing flame retardant components pursuant to the above second aspect is, in each case, at least the minimum amount of phosphorus-containing flame retardant(s) needed with the particular polymer with which such phosphorus-containing flame retardant(s) is/are blended to enable molded test specimens made from the blend to exhibit a V-0 rating in the UL-94 test procedure. Thus, more than such minimum amount relative to the amount of polymer can be used in these situations and be considered a flame retardant amount, provided that the amount of such phosphorus-containing flame retardant(s) to polymer is not so high as to make it impossible to prepare from the resultant mixture molded specimens that are substantially uniform in composition from specimen to specimen and that have acceptable properties. On the other hand, in connection with masterbatch blends or powder preblends that are prepared for future dilution with additional polymer preparatory to making finished molded, extruded or foamed shapes or objects (articles), any amount of such phosphorus-containing flame retardant(s) that is above the minimum "flame retardant amount" can be used.

Other embodiments of the invention will be still further apparent from the ensuing description and the appended claims.

FURTHER DETAILED DESCRIPTION

The First Aspect of this Invention

As noted above, this aspect of the invention involves the provision of a halogen-free flame retardant polymer composition which comprises a blend made from (a) an ABS resin, and (b) a flame retardant amount of at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less; with the provisos that (c) the ABS resin is the sole polymeric component of the composition, (d) the P,P'-dihydrocarbyl pentaerythrityl diphosphonate is, or the P,P'-dihydrocarbyl pentaerythrityl diphosphonates are, the sole phosphorus-containing flame retardant component(s) of the composition, and (e) the composition is devoid of any phosphorus-containing flame retardant synergist and any antimony-containing flame retardant synergist.

The phosphonates used in the practice of this aspect of the invention can be named in various ways: *e.g.*, as P,P'-dihydrocarbyl pentaerythrityl diphosphonates, as dihydrocarbyl pentaerythritol diphosphonates, or as dihydrocarbyl pentaerythrityl diphosphonates. The hydrocarbyl substituents on the phosphorus atoms can be the same or different, and can be saturated or unsaturated aliphatic hydrocarbyl groups, saturated or unsaturated cycloaliphatic hydrocarbyl groups, or aromatic hydrocarbyl groups, subject to the requirement that the total number of carbon atoms in the two substituents is 8 or less, *i.e.*, in the range of 2 to 8. Such hydrocarbyl groups can thus be alkyl, alkenyl, alkynyl, cycloalkyl, cycloalkenyl, cycloalkylalkyl, aryl, alkaryl, or aralkyl groups containing up to 7 carbon atoms. Thus the single aryl, alkaryl, or aralkyl group which can be present is either a phenyl, tolyl, or benzyl group, and when phenyl, the other hydrocarbyl group can have one or two carbon atoms, whereas when one group is tolyl or benzyl, the other group is methyl. Examples of symmetrical dihydrocarbyl pentaerythrityl phosphonates that may be used in the practice of this invention include dimethyl pentaerythrityl diphosphonate, diethyl pentaerythrityl diphosphonate, dipropyl pentaerythrityl diphosphonate, diisopropyl pentaerythrityl diphosphonate, dibutyl pentaerythrityl diphosphonate, diisobutyl pentaerythrityl diphosphonate, di-sec-butyl pentaerythrityl diphosphonate, di-tert-butyl pentaerythrityl diphosphonate, divinyl pentaerythrityl diphosphonate, diallyl pentaerythrityl diphosphonate, dipropenyl pentaerythrityl diphosphonate, di(2-butenyl) pentaerythrityl diphosphonate, di(2-propynyl) pentaerythrityl diphosphonate, dicyclopropylcarbinyl pentaerythrityl diphosphonate, and analogous compounds. Examples of asymmetrical dihydrocarbyl pentaerythrityl phosphonates that may be used in the practice of this invention include P-ethyl-P'-methyl pentaerythrityl diphosphonate, P-ethyl-P'-butyl pentaerythrityl diphosphonate, P-isobutyl-P'-methyl pentaerythrityl diphosphonate, P-methyl-P'-vinyl pentaerythrityl diphosphonate, P-allyl-P'-pentyl pentaerythrityl diphosphonate, P-methyl-P'-phenyl pentaerythrityl diphosphonate, P-ethyl-P'-phenyl pentaerythrityl diphosphonate, P-phenyl-P'-vinyl pentaerythrityl diphosphonate, P-ethynyl-P'-phenyl pentaerythrityl diphosphonate, P-methyl-P'-*o*-tolyl pentaerythrityl diphosphonate, P-methyl-P'-*m*-tolyl pentaerythrityl diphosphonate, P-methyl-P'-*p*-tolyl pentaerythrityl diphosphonate, P-benzyl-P'-methyl pentaerythrityl diphosphonate, P-cyclohexyl-P'-methyl pentaerythrityl diphosphonate, P-4-methylcyclohexyl-P'-methyl pentaerythrityl diphosphonate, P-cyclohex-3-enyl-P'-methyl pentaerythrityl diphosphonate, P-2-methylcyclopent-3-enyl-P'-methyl pentaerythrityl diphosphonate, and their analogs, and mixtures of two or more such compounds. Preferred from the cost-effectiveness standpoint is dimethyl pentaerythrityl diphosphonate. Methods which can

be used or adapted for use in preparing such compounds are known and reported, for example, in U.S. Pat. Nos. 3,141,032 and 4,154,721, *supra*.

When pursuant to this aspect of the invention component (b) above is blended in a flame-retardant amount into component (a) (*viz.*, an ABS resin devoid of flame retardant additive), the resultant ABS composition provides molded test specimens which exhibit a V-0 rating, if subjected to the well-known standard UL-94 test procedure.

ABS resins, methods for producing them, methods for molding, extruding and foaming them, and shapes and objects (articles) that can be made from them are all well known in the art and are reported in the literature. Anyone interested in details about any of the foregoing technology pertaining to ABS can refer, for example, to Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., Second Edition, Volume 1, copyright 1963, pages 338-351; Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., Third Edition, Volume 1, copyright 1978, pages 442-456; Kirk-Othmer, *Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc., Fourth Edition, Volume 1, copyright 1991, pages 391-411; *Encyclopedia of Polymer Science and Technology*, John Wiley and Sons, Inc., Volume 1, copyright 1964, pages 374-444; and the various other relevant publications identified on any of the foregoing cited pages of any of the foregoing encyclopedia, all such cited pages and all such other relevant publications being fully incorporated herein by reference, as if fully set forth herein. ABS resins suitable for use in the practice of this invention can be obtained from a number of commercial sources.

The following examples, in which parts per hundred parts (pph) are by weight, are presented for purposes of illustration and not limitation.

EXAMPLES 1 AND 2, AND COMPARATIVE EXAMPLES CE-3 TO CE-5

ABS (Magnum PG from Dow Chemical Co.) was blended with the additives and in the proportions (pph) shown in Table 1 by mixing in a Brabender mixer bowl at a temperature of 175°C for about 5 minutes at a rotor rate of 50-75 rpm. The formulated resin was then compression molded and cut to bar-shaped test specimens measuring 12.7 x 1.27 x ca. 0.159 centimeters (5 x 0.5 x 0.0625 inches). The specimens were then subjected to the vertical flame test according to the UL-94 procedure. Examples 1 and 2 are illustrative of this invention. Examples CE-3, CE-4, and CE-5 are presented for comparative purposes.

TABLE 1

Phosphorus Ingredient	Example 1	Example 2	CE 3	CE 4	CE 5
None (Untreated ABS)	70	75	70	70	70
5 Dimethyl pentaerythrityl phosphonate	30	25	--	--	--
Resorcinol bis(diphenylphosphate)	--	--	30	--	--
Ammonium polyphosphate	--	--	--	30	--
10 Diphenyl pentaerythrityl phosphate	--	--	--	--	30
UL-Rating	V-0	V-0*	V-2	NR	V-2
Burn Time (total of 5 samples, 2 ignitions)	< 10 sec	< 10 sec	20 sec	**	33 sec

* In one of the 10 ignitions, the sample dripped and ignited the cotton.

15 ** Some samples burned for more than 30 seconds; NR = No UL Rating.

In VICAT tests (ASTM D 1525) conducted using ca. 0.318 centimeter (1/8-inch) thick test specimens at a 1 kilogram load, it was found that the ABS compositions of Examples 1 and 2 gave temperatures of 107.7°C and 105°C as compared to 105.2°C for the untreated ABS. Thus the compositions of this invention suffered no appreciable deterioration in heat distortion properties in these tests.

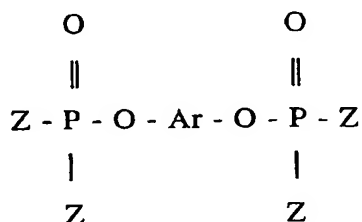
The Second Aspect of this Invention

It will be recalled that this aspect of the invention relates to a halogen-free flame retardant additive composition and its use in flame retarding various thermoplastic polymers, which additive composition comprises a blend made from (a) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbylsubstituents is 8 or less, and (b) at least one arylbis(dihydrocarbylphosphate) and/or

at least one arylbis(dihydrocarbylphosphinate) in an (a):(b) weight ratio in the range of 1:1 to 20:1, and preferably in the range of 4:1 to 6:1.

The phosphonates used in the practice of this aspect of the invention can be any one or a combination of any two or more of the phosphonates described above in connection with the first aspect of the invention.

At least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) constitute(s) the other phosphorus additive or additives used in the practice of this aspect of the invention. These compounds can be depicted by the general formula:



wherein each Z is a hydrocarbyl group which can be the same or different or is a hydrocarbyloxy group which can be the same or different, and Ar is a divalent aromatic moiety. When the Z groups are hydrocarbyl, the compound is an arylbis(dihydrocarbylphosphinate), and when the Z groups are hydrocarbyloxy, the compound is an arylbis(dihydrocarbylphosphate). Typically the hydrocarbyl groups and the hydrocarbyloxy groups each contain from 1 to 20 carbon atoms and preferably from 1 to 10 carbon atoms. Such hydrocarbyl groups can be alkyl, alkenyl, cycloalkyl, cycloalkenyl, aryl, aralkyl, cycloalkylalkyl, cycloalkylaryl or similar hydrocarbyl groups. Most preferably the hydrocarbyl groups are aryl having from 6 to 10 carbon atoms, especially phenyl. The divalent aromatic moiety, Ar, typically contains from 6 to 20 carbon atoms and can be a single ring aromatic moiety (*e.g.*, a phenylene group) or a multi-ring aromatic moiety such as a biphenylene group (*e.g.*, -C₆H₄-C₆H₄-), naphthylene group (*e.g.*, -C₁₀H₆-), an oxybiphenylene group (*e.g.*, -C₆H₄-O-C₆H₄-), an alkylenebiphenylene group (*e.g.*, -C₆H₄-R-C₆H₄- where R is an alkylene group 1 to 4 carbon atoms in length and having a total from 1 to 6 carbon atoms), or the like. The foregoing moieties can be substituted by one or hydrocarbyl groups, such as alkyl. The arylbis(dihydrocarbylphosphates) are exemplified by such compounds as resorcinolbis(dimethylphosphate), resorcinolbis(diethylphosphate), resorcinolbis(dipropyl-phosphate), resorcinolbis(dibutylphosphate), resorcinolbis(dioctylphosphate), resorcinolbis(divinylphosphate), resorcinolbis(diallylphosphate), resorcinol-

bis(dicyclohexylphosphate), resorcinolbis(dimethylcyclohexylphosphate), resorcinol-
 bis(dicyclohexenylphosphate), resorcinolbis(dimethylcyclohexenylphosphate), resorcinol-
 bis(ditolylphosphate), resorcinolbis(dixylylphosphate), resorcinolbis(diethylphenylphosphate),
 resorcinolbis(di-1-naphthylphosphate), resorcinolbis(di-2-naphthylphosphate), resorcinolbis(di-
 5 benzylphosphate), resorcinolbis(di-2-methylbenzylphosphate), resorcinolbis(di-3-
 methylbenzylphosphate), resorcinolbis(di-4-methylbenzylphosphate), resorcinolbis(diphen-
 ethylphosphate), resorcinolbis(di- α -methylbenzylphosphate), resorcinolbis(dicyclopropyl-
 carbinylphosphate), hydroquinonebis(dimethylphosphate), hydroquinonebis(diethylphosphate),
 hydroquinonebis(dipropylphosphate), hydroquinonebis(dibutylphosphate), hydroquinonebis(di-
 10 octylphosphate), hydroquinonebis(divinylphosphate), hydroquinonebis(diallylphosphate),
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 hydroquinonebis(ditolylphosphate), hydroquinonebis(dixylylphosphate), hydroquinone-
 bis(diethylphenylphosphate), hydroquinonebis(di-1-naphthylphosphate), hydroquinonebis(di-2-
 15 naphthylphosphate), hydroquinonebis(dibenzylphosphate), hydroquinonebis(di-2-methyl-
 benzylphosphate), hydroquinonebis(di-3-methylbenzylphosphate), hydroquinonebis(di-4-
 methylbenzylphosphate), hydroquinonebis(diphenethylphosphate), hydroquinonebis(di- α -
 methylbenzylphosphate), hydroquinonebis(dicyclopropylcarbinylphosphate), catechol-
 bis(dimethylphosphate), catecholbis(diethylphosphate), catecholbis(dipropylphosphate),
 20 catecholbis(dibutylphosphate), catecholbis(dioctylphosphate), catecholbis(divinylphosphate),
 catecholbis(diallylphosphate), catecholbis(dicyclohexylphosphate), catecholbis(di-
 methylcyclohexylphosphate), catecholbis(dicyclohexenylphosphate), catecholbis(di-
 methylcyclohexenylphosphate), catecholbis(ditolylphosphate), catecholbis(dixylylphosphate),
 catecholbis(diethylphenylphosphate), catecholbis(di-1-naphthylphosphate), catecholbis(di-2-
 25 naphthylphosphate), catecholbis(dibenzylphosphate), catecholbis(di-2-methylbenzylphosphate),
 catecholbis(di-3-methylbenzylphosphate), catecholbis(di-4-methylbenzylphosphate), catechol-
 bis(diphenethylphosphate), catecholbis(di- α -methylbenzylphosphate), catecholbis(dicyclo-
 propylcarbinylphosphate), 1,1'-oxydiphenol-4,4'-bis(dimethylphosphate), 1,1'-oxydiphenol-4,4'-
 bis(diethylphosphate), 1,1'-oxydiphenol-4,4'-bis(dibutylphosphate), 1,1'-oxydiphenol-4,4'-
 30 bis(diphenylphosphate), 1,1'-oxydiphenol-3,3'-bis(dimethylphosphate), 1,1'-oxydiphenol-3,3'-
 bis(diphenylphosphate), 1,1'-oxydiphenol-3,3'-bis(diallylphosphate), 1,1'-oxydiphenol-3,3'-
 bis(dicyclohexylphosphate), 1,1'-oxydiphenol-2,2'-bis(dimethylphosphate), 1,1'-oxydiphenol-2,2'-
 bis(dicyclohexenylphosphate), 1,1'-oxydiphenol-2,2'-bis(diphenylphosphate), methylenebisphenol-

bis(dimethylphosphate), methylenebisphenolbis(diphenylphosphate), methylenebisphenolbis(dibenzylphosphate), 4,4'-methylenebis(m-cresol)bis(diphenylphosphate), 4,4'-methylenebis(o-cresol)bis(diphenylphosphate), 4,4'-methylenebis(m-cresol)bis(dimethylphosphate), 4,4'-methylenebis(o-cresol)bis(dimethylphosphate), 4,4'-methylenebis(m-cresol)bis(dibenzylphosphate), 4,4'-methylenebis(o-cresol)bis(dibenzylphosphate), 2,2'-propylidenebisphenolbis(dimethylphosphate) (a.k.a. bisphenol-A-dimethylphosphate), 2,2'-propylidenebisphenolbis(diphenylphosphate) (a.k.a. bisphenol-A-diphenylphosphate), 2,2'-propylidenebisphenolbis(dibenzylphosphate) (a.k.a. bisphenol-A-dibenzylphosphate), 2,2'-propylidenebis(m-cresol)bis(diphenylphosphate), 2,2'-propylidenebis(o-cresol)bis(diphenylphosphate), 2,2'-propylidenebis(m-cresol)bis(dimethylphosphate), 2,2'-propylidenebis(o-cresol)bis(dimethylphosphate), 2,2'-propylidenebis(m-cresol)bis(dibenzylphosphate), 2,2'-propylidenebis(o-cresol)bis(dibenzylphosphate), 1,1'-ethylidenebisphenolbis(diphenylphosphate), 1,1'-propylidenebisphenolbis(diphenylphosphate), benzylidenebis(diphenylphosphate), and analogous compounds.

Typical examples of the arylbis(dihydrocarbylphosphinates) useful in the practice of this aspect of the invention include: resorcinolbis(dimethylphosphinate), resorcinolbis(diethylphosphinate), resorcinolbis(dipropylphosphinate), resorcinolbis(dibutylphosphinate), resorcinolbis(dioctylphosphinate), resorcinolbis(divinylphosphinate), resorcinolbis(diallylphosphinate), resorcinolbis(dicyclohexylphosphinate), resorcinolbis(dimethylcyclohexylphosphinate), resorcinolbis(dicyclohexenylphosphinate), resorcinolbis(dimethylcyclohexenylphosphinate), resorcinolbis(ditolylphosphinate), resorcinolbis(dixylylphosphinate), resorcinolbis(diethylphenylphosphinate), resorcinolbis(di-1-naphthylphosphinate), resorcinolbis(di-2-naphthylphosphinate), resorcinolbis(dibenzylphosphinate), resorcinolbis(di-2-methylbenzylphosphinate), resorcinolbis(di-3-methylbenzylphosphinate), resorcinolbis(di-4-methylbenzylphosphinate), resorcinolbis(di-phenethylphosphinate), resorcinolbis(di- α -methylbenzylphosphinate), resorcinolbis(dicyclopropylcarbonylphosphinate), hydroquinonebis(dimethylphosphinate), hydroquinonebis(diethylphosphinate), hydroquinonebis(dipropylphosphinate), hydroquinonebis(dibutylphosphinate), hydroquinonebis(dioctylphosphinate), hydroquinonebis(divinylphosphinate), hydroquinonebis(diallylphosphinate), hydroquinonebis(dicyclohexylphosphinate), hydroquinonebis(dimethylcyclohexylphosphinate), hydroquinonebis(dicyclohexenylphosphinate), hydroquinonebis(dimethylcyclohexenylphosphinate), hydroquinonebis(ditolylphosphinate), hydroquinonebis(dixylylphosphinate), hydroquinonebis(diethylphenylphosphinate), hydroquinonebis(di-1-naphthylphosphinate), hydroquinonebis(di-2-

naphthylphosphinate), hydroquinonebis(dibenzylphosphinate), hydroquinonebis(di-2-methylbenzylphosphinate), hydroquinonebis(di-3-methylbenzylphosphinate), hydroquinonebis(di-4-methylbenzylphosphinate), hydroquinonebis(di-phenethylphosphinate), hydroquinonebis(di- α -methylbenzylphosphinate), hydroquinonebis(dicyclopropylcarbinylphosphinate), catecholbis(dimethylphosphinate), catecholbis(diethylphosphinate), catecholbis(dipropylphosphinate), catecholbis(dibutylphosphinate), catecholbis(dioctylphosphinate), catecholbis(divinylphosphinate), catecholbis(diallylphosphinate), catecholbis(dicyclohexylphosphinate), catecholbis(dimethylcyclohexylphosphinate), catecholbis(dicyclohexenylphosphinate), catecholbis(dimethylcyclohexenylphosphinate), catecholbis(ditolylphosphinate), catecholbis(dixylylphosphinate), catecholbis(diethylphenylphosphinate), catecholbis(di-1-naphthylphosphinate), catecholbis(di-2-naphthylphosphinate), catecholbis(dibenzylphosphinate), catecholbis(di-2-methylbenzylphosphinate), catecholbis(di-3-methylbenzylphosphinate), catecholbis(di-4-methylbenzylphosphinate), catecholbis(di-phenethylphosphinate), catecholbis(di- α -methylbenzylphosphinate), catecholbis(dicyclopropylcarbinylphosphinate), 1,1'-oxydiphenol-4,4'-bis(dimethylphosphinate), 1,1'-oxydiphenol-4,4'-bis(diethylphosphinate), 1,1'-oxydiphenol-4,4'-bis(dibutylphosphinate), 1,1'-oxydiphenol-4,4'-bis(diphenylphosphinate), 1,1'-oxydiphenol-3,3'-bis(dimethylphosphinate), 1,1'-oxydiphenol-3,3'-bis(diphenylphosphinate), 1,1'-oxydiphenol-3,3'-bis(diallylphosphinate), 1,1'-oxydiphenol-3,3'-bis(dicyclohexylphosphinate), 1,1'-oxydiphenol-2,2'-bis(dimethylphosphinate), 1,1'-oxydiphenol-2,2'-bis(dicyclohexenylphosphinate), 1,1'-oxydiphenol-2,2'-bis(diphenylphosphinate), methylenebisphenolbis(dimethylphosphinate), methylenebisphenolbis(diphenylphosphinate), methylenebisphenolbis(dibenzylphosphinate), 4,4'-methylenebis(m-cresol)bis(diphenylphosphinate), 4,4'-methylenebis(o-cresol)bis(diphenylphosphinate), 4,4'-methylenebis(m-cresol)bis(dimethylphosphinate), 4,4'-methylenebis(o-cresol)bis(dimethylphosphinate), 4,4'-methylenebis(m-cresol)bis(dibenzylphosphinate), 4,4'-methylenebis(o-cresol)bis(dibenzylphosphinate), 2,2'-propylidenebisphenolbis(dimethylphosphinate) (a.k.a. bisphenol-A-dimethylphosphinate), 2,2'-propylidenebisphenolbis(diphenylphosphinate) (a.k.a. bisphenol-A-diphenylphosphinate), 2,2'-propylidenebisphenolbis(dibenzylphosphinate) (a.k.a. bisphenol-A-dibenzylphosphinate), 2,2'-propylidenebis(m-cresol)bis(diphenylphosphinate), 2,2'-propylidenebis(o-cresol)bis(diphenylphosphinate), 2,2'-propylidenebis(m-cresol)bis(dimethylphosphinate), 2,2'-propylidenebis(o-cresol)bis(dimethylphosphinate), 2,2'-propylidenebis(m-cresol)bis(dibenzylphosphinate), 2,2'-propylidenebis(o-cresol)bis(dibenzylphosphinate), 1,1'-ethylidenebisphenolbis(diphenylphosphinate), 1,1'-propylidenebisphenolbis(diphenylphosphinate), benzylidenebis(diphenylphosphinate), and analogous compounds.

For ease of reference, hereinafter the P,P'-dihydrocarbyl pentaerythrityl diphosphonates are sometimes referred to generally as "phosphonate", the arylbis(dihydrocarbylphosphates) are sometimes referred to generally as "phosphate", and the arylbis(dihydrocarbylphosphinates) are sometimes referred to generally as "phosphinate".

5 The relative proportions of phosphonate (a), to phosphate and/or phosphinate (b) are typically in the range of 1 to 20 parts by weight of phosphonate per part by weight of phosphate and/or phosphinate (b). Preferably the (a):(b) weight ratio is in the range of 1 to 10 parts of (a) per part of (b). The (a):(b) weight ratio is more preferably in the range of 4 to 6 parts of (a) per part of (b). A ratio of 5 parts of (a) per part by weight of (b) is most preferred. When (b)
10 is a combination of phosphate and phosphinate, the relative proportions between the phosphate and phosphinate can range anywhere in the range of from a trace of one to a trace of the other. In other words, the phosphate and the phosphinate can be used together in any and all proportions relative to each other.

Thermoplastic polymers with which the additives of this invention can be blended include
15 such polymers as polystyrene; copolymers of two or more styrenic monomers such as styrene, vinyltoluene, ethylstyrene, tert-butylstyrene, α -methylstyrene, vinylnaphthalene, etc.; rubber-modified vinylaromatic homopolymers or copolymers (*e.g.*, high impact polystyrene); ABS, thermoplastic polyesters such as polyethylene terephthalate, polybutylene terephthalate, polytrimethylene terephthalate, polycyclohexylene terephthalate, etc., thermoplastic polyamides,
20 such as nylon 6, nylon 66, nylon 6,12, etc.; polycarbonates, polyphenylene oxides, such as poly(2,6-dimethylphenylene oxide); polysulphones; polyolefins, such as polyethylene, polypropylene, poly-(1-butene), copolymers of ethylene with one or more higher vinyl olefins such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene; and blends or composites of different polymers such as for example a blend of poly(2,6-dimethylphenylene oxide) and
25 polystyrene, and similar substances. A large number of additive-free thermoplastic polymers suitable for use in the practice of this aspect of the invention can be obtained from a number of commercial sources. Preferred thermoplastic polymers for use in the practice of this aspect of the invention are ABS and styrenic polymers, especially high impact polystyrene.

The ABS polymer compositions of this aspect of the invention can be in the form of a
30 preblend (*e.g.*, a powder blend) of components (a) and (b), which can be molded or extruded under suitable temperature and pressure conditions to form a shape or object, whether foamed (expanded) in non-foamed (non-expanded) condition. Likewise the compositions can be in the form of the molded or extruded shape or object itself. Also, the ABS polymer compositions of

this aspect of the invention can be in the form of a masterbatch or concentrated preblend in which the concentration of component (b) therein is higher than its intended concentration in the ultimate finished molded shape or object to be fabricated. Such masterbatch or concentrated preblend is mixed or blended with additional ABS either as dry materials or as a melt blend which is then molded or extruded to produce the finished shape or object.

The polymer compositions of this aspect of the invention can be in the form of a preblend (e.g., a powder blend) of (A) at least one phosphonate, and (B) at least one phosphate or (C) at least one phosphinate, or (D) a combination of at least one phosphate and at least one phosphinate, which can be molded or extruded under suitable temperature and pressure conditions to form a shape or object, whether foamed (expanded) or in non-foamed (non-expanded) condition. Likewise the compositions can be in the form of the molded or extruded shape or object itself. Also, the polymer compositions of this aspect of the invention can be in the form of a masterbatch or concentrated preblend in which the concentration of the flame retardant components therein is higher than the intended concentration in the ultimate finished molded shape or object to be fabricated. Such masterbatch or concentrated preblend is mixed or blended with additional polymer either as dry materials or as a melt blend which is then molded or extruded to produce the finished shape or object.

When pursuant to this second aspect of the invention the flame retardant components above are blended in a flame-retardant amount into the thermoplastic polymer (i.e., a thermoplastic polymer devoid of any halogen-containing flame retardant additive, and preferably devoid of any antimony-containing additive component as well), the resultant polymer composition provides molded test specimens which exhibit a V-0 rating, if subjected to the well-known standard UL-94 test procedure. In forming the blends the individual flame retardants can be separately blended with the substrate polymer. Preferably however, a preformed mixture of (A) at least one phosphonate, and (B) at least one phosphate or (C) at least one phosphinate, or (D) a combination of at least one phosphate and at least one phosphinate is employed in the blending operation. In this way the likelihood of blending errors is reduced, and in general the blending operation is rendered more facile.

The following examples pertaining to the second aspect of this invention and in which parts per hundred parts (pph) are by weight, are presented for purposes of illustration and not limitation.

EXAMPLES 3 TO 5, AND COMPARATIVE EXAMPLES CE-6 TO CE-9

ABS (Magnum PG from Dow Chemical Co.) was blended with the additives and in the proportions (pph) shown in Table 2 by mixing in a Brabender mixer bowl at a temperature of 175°C for about 5 minutes at a rotor rate of 50-75 rpm. The formulated resin was then compression molded and cut to bar-shaped test specimens measuring 12.7 x 1.27 x ca. 0.159 centimeters (5 x 0.5 x 0.0625 inches). The specimens were then subjected to the vertical flame test according to the UL-94 procedure. Examples 3-5 are illustrative of this invention. Examples CE-6 through CE-9 are presented for comparative purposes.

TABLE 2

Ingredient	Ex. 3	Ex. 4	Ex. 5	CE-6	CE-7	CE-8	CE-9
ABS	70	70	70	70	75	70	70
Pentaerythrityl dimethylphosphonate	25	25	25	30	25	--	--
Resorcinol bis-(diphenylphosphate)	5	--	--	--	--	30	15
Resorcinol bis(di-phenylphosphinate)	--	5	--	--	--	--	--
Bisphenol-A-bis-(diphenylphosphate)	--	--	5	--	--	--	--
Triphenylphosphate	--	--	--	--	--	--	15
UL-Rating	V-0	V-0	V-0	V-0	V-0*	V-2	V-2
Burn Time (total of 5 samples, 2 ignitions)	< 10sec	< 10sec	< 10sec	< 10sec	< 10sec	20sec	12sec

EXAMPLES 6 AND 7, AND COMPARATIVE EXAMPLES CE-9 TO CE-12

A number of test specimens were prepared from various formulations as in Examples 1-3 and subjected to standard physical property determinations. The materials tested and the test results are summarized in Table 3. Examples 6 and 7 illustrate the present invention. Examples

CE-9 through CE-12 are presented for comparative purposes. The flame retardant used in Example CE-12 is a well known commercially accepted halogen-containing and antimony-containing flame retardant system.

TABLE 3

Physical Property	Ex. 6	Ex. 7	CE-9	CE-10	CE-11	CE-12
ABS	75	75	70	75	100	72
Pentaerythrityl dimethylphosphonate	20	15	30	25	--	--
Resorcinol bis(diphenylphosphate)	5	10	--	--	--	--
Tetrabromobisphenol A (24%) & Sb ₂ O ₃ (4%)	--	--	--	--	--	28
IZOD 1/8", (ft-lb/in)	0.99	0.99	0.44	0.56	2.27	0.95
VICAT (deg C)	94	81	107.7	105	105.2	88.8

Both Aspects of the Invention

The flame retarded polymer compositions of the respective aspects of this invention can constitute finished polymer compositions containing a flame retardant amount of the particular flame retardant(s) of that particular aspect in the range of 3 to 50 weight percent, although it is more desirable in most cases that this upper amount be 40 weight percent (so that the composition contains a flame retardant amount in the range of 3 to 40 weight percent), and even more desirable in most cases that this upper amount be 30 weight percent (so that the composition contains a flame retardant amount in the range of 3 to 30 weight percent). Preferably the finished composition contains in the range of 10 to 40 weight percent, and most preferably in the range of 20 to 30 weight percent of the applicable phosphorus-containing flame retardant(s) for the particular aspect in whatever chemical form and composition such flame retardant exists or such flame retardants exist after being blended into a substrate resin of the particular aspect, such weight percentage being based on the total weight of the applicable resin plus the applicable phosphorus-containing flame retardant(s) used in forming the blended composition, and excluding the weight of other components, if any, used in forming the finished polymer composition. As noted above, one way of forming such polymer compositions is by use of masterbatch or additive-rich preblend compositions made from an applicable substrate

resin and a higher percentage of the applicable phosphorus-containing flame retardant(s) than the percentage to be included in the ultimate finished product. Such masterbatches or additive-rich preblend compositions will typically be a melt blended masterbatch or a powder preblend made from 20 to 90 parts by weight of the applicable phosphorus-containing flame retardant(s) per hundred parts by weight substrate resin plus the phosphorus-containing flame retardant(s) being used. Such masterbatch and additive-rich preblend compositions, which constitute additional embodiments of this invention, can subsequently be used in forming finished polymer compositions by blending an appropriate amount of the masterbatch or additive-rich preblend with an appropriate amount of the same substrate resin which does not contain any flame retardant component to thereby produce a blend having the desired end use proportions of the substrate resin and the phosphorus-containing flame retardant(s) being used in whatever form they exist after being blended together. It is to be kept in mind that in the case of the first aspect of this invention, the ABS resin is the sole polymeric component of the composition, and the dihydrocarbyl pentaerythrityl diphosphonate is, or the dihydrocarbyl pentaerythrityl diphosphonates are, the sole phosphorus-containing component(s) of the composition. Also, it should be kept in mind that in the second aspect of the invention the flame retardant used is a combination of (1) at least one dihydrocarbyl pentaerythrityl diphosphonate and (2) at least one arylbis(dihydrocarbylphosphate) or at least one arylbis(dihydrocarbylphosphinate) or at least one arylbis(dihydrocarbylphosphate) plus at least one arylbis(dihydrocarbylphosphinate), and that the substrate polymer or resin is a single thermoplastic polymer or a blend of thermoplastic polymers.

No halogen-containing additive component is intentionally added to the compositions of this invention. Consequently, the polymer compositions of this invention do not contain halogen except for impurities which may occur therein as a consequence of the materials (solvents, catalysts, *etc.*), process or process equipment used in their synthesis or manufacture. Typically the additive compositions, *e.g.*, a masterbatch or preblend of the flame retardant component(s), which can be used in accordance with this invention to prepare the finished polymer compositions of this invention, will contain, if any, no more than about 1000 parts by weight of halogen impurities per million parts by weight (ppmw) of additive composition, and thus the term "halogen-free" in connection with such additive compositions means that they contain, if any, no more than about 1000 ppmw of halogen. The finished polymer compositions of this invention will typically contain, if any, no more than about 100 parts by weight of halogen impurities per million parts by weight of the total polymer composition. Therefore, the term "halogen-free"

as used herein in connection with the finished polymer compositions means that they contain, if any, no more than about 100 ppmw of halogen. Usually they will contain less halogen than this, unless a halogen-containing solvent or a halogen-containing gas is used in preparing the resin or a foam produced from a polymer composition of this invention.

5 Similarly, in preferred embodiments no antimony-containing additive is intentionally added to a composition of this invention. Such preferred compositions are devoid of antimony-containing components except possibly for adventitious trace amounts which possibly may find their way into the polymer blends through contamination of blending equipment by antimony additives such as antimony oxides previously used in such equipment.

10 Further embodiments of this invention are the methods of rendering an applicable substrate polymer flame resistant which comprises incorporating therein the applicable phosphorus-containing flame retardant(s) in an amount such that the resultant polymer composition contains a flame retardant amount of the applicable flame retardant(s) in whatever chemical composition and form such components exist in the resultant polymer composition. As
15 noted above, such polymer composition can provide test specimens exhibiting V-0 rating in the UL-94 test procedure. It is possible to incorporate the applicable flame retardant(s) of this invention in an applicable substrate polymer prior to, or during, formation of the polymer. For example, such components may possibly be added to the monomer(s) or to the polymerization system to be used in forming the polymer. Similarly, it may be possible to add the flame
20 retardant(s) to the polymerization mixture during the course of the polymerization reaction itself. Preferably however, the flame retardant(s) of the invention is/are added to the applicable thermoplastic polymer after the polymer has been produced. It will also be appreciated that the possibility exists for additions being made in stages, such as prior to and during the polymerization, or prior to and after the polymerization, or during and after the polymerization,
25 or prior to, during and after the polymerization.

Other ingredients such as extrusion aids (*e.g.*, barium stearate or calcium stearate), acid scavengers (*e.g.*, magnesium oxide or tetrasodium pyrophosphate), dyes, pigments, fillers, stabilizers, antioxidants, antistatic agents, reinforcing agents, and the like can be included in the polymer compositions of this invention. Nucleating agents (*e.g.*, talc, calcium silicate, or
30 indigo) to control cell size are desirably included in the polymer compositions of this invention designed for producing expanded or foamed polymeric materials. The particular materials selected for use in the composition of this invention should not materially affect adversely the properties of the finished polymer composition for its intended utility.

Various known procedures can be used to prepare the blends or formulations constituting the compositions of this aspect of the invention. For example the components to be incorporated into the finished blend can be blended together in powder form and thereafter molded by extrusion, compression, or injection molding. Likewise the components can be mixed together
5 in a Banbury mixer, a Brabender mixer, a roll mill, a kneader, or other similar mixing device, and then formed into the desired form or configuration such as by extrusion followed by comminution into granules or pellets, or by other known methods.

The compositions of this invention can be utilized in the formation of useful articles of the type normally fabricated by molding or extrusion of conventional flame retarded polymers.
10 Likewise it is possible to prepare foamed or expanded shapes and objects from the compositions of this invention. Molding and extrusion conditions such as temperatures and pressures are within conventional recommended limits. Conditions normally used for producing foamed or expanded shapes and objects from flame retarded thermoplastic polymers can be used with the compositions of this invention, with little or no modification.

15 It is to be understood that each component or ingredient referred to anywhere in the specification or claims hereof, whether referred to in the singular or plural, identifies the substance in the chemical form and composition as it exists at least prior to inclusion, mixing or blending with one or more other ingredients or components. It matters not what chemical changes, transformations and/or reactions, if any, take place in the mixture itself as such
20 changes, transformations and/or reactions are the natural result of bringing the specified components or ingredients together under the conditions called for pursuant to this disclosure. It is also to be understood that even though the claims hereinafter may refer to substances in the present tense (*e.g.*, "comprises" or "is"), the reference is to the substance, as it existed at the time just before it was first contacted, blended or mixed with one or more other substances in
25 accordance with the present disclosure. The fact that a substance may lose its original identity through a chemical reaction, complex formation, solvation, ionization, or other transformation during the course of contacting, blending or mixing operations, if done in accordance with the disclosure hereof, is within the purview and scope of this invention.

THAT WHICH IS CLAIMED IS:

1. A halogen-free flame retardant polymer composition which comprises:

I) a blend made from:

a) an ABS resin, and

b) a flame retardant amount of at least one P,P'-dihydrocarbyl pentaerythrityl
5 diphosphonate in which the total number of carbon atoms in the two hydrocarbyl
substituents is 8 or less;

with the provisos that:

c) the ABS resin is the sole polymeric component of said composition,

d) the P,P'-dihydrocarbyl pentaerythrityl diphosphonate is, or the P,P'-dihydrocarbyl
10 pentaerythrityl diphosphonates are, the sole phosphorus-containing flame retardant
component(s) of said composition, and

e) said composition is devoid of any phosphorus-containing flame retardant synergist
and any antimony-containing flame retardant synergist; or

II) a blend made from:

f) at least one thermoplastic polymer, and

g) a flame retardant amount of a combination of (i) at least one P,P'-
15 dihydrocarbyl pentaerythrityl diphosphonate in which the total number of
carbon atoms in the two hydrocarbyl substituents is 8 or less, and (ii) at
least one arylbis(dihydrocarbylphosphate) and/or at least one
20 arylbis(dihydrocarbylphosphinate) in an (i):(ii) weight ratio in the range of
1:1 to 20:1.

2. A composition according to Claim 1 wherein said blend is made from a) and b)
subject to the provisos c), d), and e).

3. A composition according to Claim 1 wherein said blend is made from f) and g).

4. A composition according to any of Claims 1-3 wherein said amount is 30 weight
25 percent or less.

5. A composition according to any of Claims 1-3 wherein said composition is a melt
blended masterbatch or a powder preblend.

6. A molded, extruded, foamed, or expanded shape or object made from a
30 composition of any of Claims 1-3.

7. A shape or object according to Claim 6 wherein the diphosphonate used in forming said composition is dimethyl pentaerythrityl diphosphonate, and wherein the amount of said diphosphonate used in making the composition is 30 weight percent or less.

8. A composition of Claim 1 or 2 wherein the weight ratio of a):b) on a weight basis is in the range of 70:30 to 75:25.

9. A composition according to Claim 3 wherein (ii) is at least one arylbis(dihydrocarbylphosphate).

10. A composition according to Claim 3 wherein (ii) is resorcinol bis(diphenylphosphate).

11. A composition according to Claim 3 wherein (ii) is 2,2'-propylidenebisphenolbis(diphenylphosphate).

12. A composition according to Claim 3 wherein (ii) is at least one arylbis(dihydrocarbylphosphinate).

13. A composition according to Claim 3 wherein (ii) is resorcinol bis(diphenylphosphinate).

14. A composition according to any of Claims 1-4, or 8-13 wherein the diphosphonate used in forming said blend is dimethyl pentaerythrityl diphosphonate.

15. A composition according to Claim 3 wherein f) is a vinylaromatic polymer.

16. A composition according to Claim 3 wherein f) is high-impact polystyrene.

17. A composition according to Claim 3 wherein f) is ABS.

18. A composition according to any of Claims 3, 9-13, or 15-17 wherein said composition is antimony-free.

19. A molded, extruded, foamed, or expanded shape or object made from a composition of any of Claims 3, 9-13, or 15-17.

20. A composition according to any of Claims 1, 3, 9-13, or 15-17 wherein said (i):(ii) weight ratio is in the range of 4:1 to 6:1.

21. A composition according to any of Claims 3, 9-13, or 15-17 wherein f) is polystyrene, a copolymer of two or more styrenic monomers, a rubber-modified vinylaromatic homopolymer or copolymer, or ABS.

22. A composition according to Claim 21 wherein said (i):(ii) weight ratio is in the range of 4:1 to 6:1.

23. A method of forming a halogen-free flame retardant polymer composition which comprises:

I) blending together:

- a) an ABS resin which is free of any (1) halogen-containing flame retardant, (2) phosphorus-containing flame retardant, and (3) phosphorus-containing or antimony-containing flame retardant synergist, and
- b) a flame retardant amount of a P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less, or a combination of more than one such diphosphonate; so that:
- c) the ABS resin is the sole polymeric component of said composition,
- d) the P,P'-dihydrocarbyl pentaerythrityl diphosphonate is, or the P,P'-dihydrocarbyl pentaerythrityl diphosphonates are, the sole phosphorus-containing flame retardant component(s) of said composition, and
- e) said composition is devoid of any phosphorus-containing flame retardant synergist and any antimony-containing flame retardant synergist; or

II) blending together:

- f) a thermoplastic polymer, and
- g) a flame retardant amount of a combination of (i) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less, and (ii) at least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) in an (i):(ii) weight ratio in the range of 1:1 to 20:1, such that said blend is free from any halogen-containing flame retardant.

24. A method according to Claim 23 wherein said composition is formed by blending together a) and b) in accordance with the terms of c), d), and e).

25. A method according to Claim 23 wherein said composition is formed by blending together f) and g).

26. A method according to any of Claims 23-25 wherein the blending is accomplished while the polymer being used is in the form of a molten polymer.

27. A method according to any of Claims 23-25 wherein the polymer and the phosphorus-containing flame retardant(s) being used are in the form of powders or granules and wherein the blending is accomplished while the polymer and the phosphorus-containing flame retardant(s) being used are in the form of powders or granules.

28. A method according to Claim 25 wherein (ii) is resorcinol bis(diphenylphosphate), resorcinol bis(diphenylphosphinate), or 2,2'-propylidenebisphenolbis(diphenylphosphate).

29. A method according to any of Claims 23-25 or 28 wherein the diphosphonate used is dimethyl pentaerythrityl diphosphonate.

5 30. A method of producing a flame retarded molded shape or object, which method comprises molding:

I) a halogen-free blended composition made from:

- a) an ABS resin, and
- b) a flame retardant amount of at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less;

with the provisos that:

- c) the ABS resin is the sole polymeric component of said composition,
- d) the P,P'-dihydrocarbyl pentaerythrityl diphosphonate is, or the P,P'-dihydrocarbyl pentaerythrityl diphosphonates are, the sole phosphorus-containing flame retardant component(s) of said composition, and
- e) said composition is devoid of any phosphorus-containing flame retardant synergist and any antimony-containing flame retardant synergist; or

II) a halogen-free blended composition made from:

- f) a thermoplastic polymer, and
- g) a flame retardant amount of a combination of (i) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less and (ii) at least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) in an (i):(ii) weight ratio in the range of 1:1 to 20:1, such that said blend is free from any halogen-containing flame retardant.

31. A method according to Claim 30 wherein said shape or object is produced by molding a) and b) in accordance with the terms of c), d), and e).

32. A method according to Claim 30 wherein said shape or object is produced by molding f) and g).

33. A method according to Claim 32 wherein (ii) is resorcinol bis(diphenylphosphate), resorcinol bis(diphenylphosphinate), or 2,2'-propylidenebisphenolbis(diphenylphosphate).

34. A method according to any of Claims 30-33 wherein the diphosphonate used is dimethyl pentaerythrityl diphosphonate.

35. A method of producing a flame retarded extruded shape or object, which method comprises expressing through a die a molten halogen-free composition made from:

- 5 I) a blend comprising:
- a) an ABS resin, and
 - b) a flame retardant amount of at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less;

10 with the provisos that:

- c) the ABS resin is the sole polymeric component of said composition,
- d) the P,P'-dihydrocarbyl pentaerythrityl diphosphonate is, or the P,P'-dihydrocarbyl pentaerythrityl diphosphonates are, the sole phosphorus-containing flame retardant component(s) of said composition, and
- 15 e) said composition is devoid of any phosphorus-containing flame retardant synergist and any antimony-containing flame retardant synergist; or

II) a blend comprising:

- f) a thermoplastic polymer, and
 - g) a flame retardant amount of a combination of (i) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less and (ii) at least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) in a (i):(ii) weight ratio of in the range of 1:1 to 20:1, such that said blend is free from any halogen-containing flame retardant.
- 25

36. A method according to Claim 35 wherein said shape or object is produced using a blend of a) and b) in accordance with the terms of c), d), and e).

37. A method according to Claim 35 wherein said shape or object is produced using a blend of f) and g).

30 38. A method according to Claim 37 wherein (ii) is resorcinol bis(diphenylphosphate), resorcinol bis(diphenylphosphinate), or 2,2'-propylidenebisphenolbis(diphenylphosphate).

39. A method according to Claim 37 wherein f) is high impact polystyrene or ABS.

40. A method according to any of Claims 35-39 wherein the diphosphonate used is dimethyl pentaerythrityl diphosphonate.

41. A method according to any of Claims 23, 25, 28, 30, 32, 33, 35, or 37-39 wherein said (i):(ii) weight ratio is in the range of 4:1 to 6:1.

5 42. A method according to Claim 41 wherein f) is polystyrene, a copolymer of two or more styrenic monomers, a rubber-modified vinylaromatic homopolymer or copolymer, or ABS.

43. A halogen-free flame retardant additive composition which comprises a blend made from (i) at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total
10 number of carbon atoms in the two hydrocarbyl substituents is 8 or less, and (ii) at least one arylbis(dihydrocarbylphosphate) and/or at least one arylbis(dihydrocarbylphosphinate) in an (i):(ii) weight ratio in the range of 1:1 to 20:1.

44. A composition according to Claim 43 wherein said blend is made from at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in
15 the two hydrocarbyl substituents is 8 or less, and at least one arylbis(dihydrocarbylphosphate).

45. A composition according to Claim 43 wherein said blend is made from at least one P,P'-dihydrocarbyl pentaerythrityl diphosphonate in which the total number of carbon atoms in the two hydrocarbyl substituents is 8 or less, and at least one arylbis(dihydrocarbylphosphinate).

46. A composition according to Claim 43 wherein (ii) is resorcinol
20 bis(diphenylphosphate), resorcinol bis(diphenylphosphinate), or 2,2'-propylidenebisphenolbis(diphenylphosphate).

47. A composition according to any of Claims 43-46 wherein (i) is pentaerythrityl dimethyl phosphonate.

48. A composition according to any of Claims 43-46 wherein said composition is
25 antimony-free.

49. A composition according Claim 48 wherein (i) is pentaerythrityl dimethyl phosphonate.

50. A composition according to any of Claims 43-46 wherein the (i):(ii) weight ratio is in the range of 4:1 to 6:1.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/20847

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08K5/51 C08L55/02 //(C08K5/51,5:5333,5:521)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 684 250 A (GREAT LAKES CHEMICAL ITALIA) 29 November 1995 (1995-11-29) page 8, line 12; table 1 ---	1,2,23, 24,30, 31,41,42
A	EP 0 176 774 A (BASF AG) 9 April 1986 (1986-04-09) example 9; tables ---	1,3,14, 17,18, 21,23, 25,29, 30,32,34
A	EP 0 176 775 A (BASF AG) 9 April 1986 (1986-04-09) example 9; table 2 ---	1,3,14, 17,18, 21,23, 25,29, 30,32,34
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

9 February 2000

Date of mailing of the international search report

16/02/2000

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INTERNATIONAL SEARCH REPORT

Inter national Application No

PCT/US 99/20847

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 4 162 278 A (GRANZOW ALBRECHT H) 24 July 1979 (1979-07-24) cited in the application</p> <p>column 2, line 37 - line 41; claims 1-7,9 -----</p>	<p>1,3,14, 16,18, 21,23, 25,29, 30,32,34</p>
A	<p>US 4 228 063 A (GRANZOW ALBRECHT H) 14 October 1980 (1980-10-14) example 6; table II -----</p>	<p>1,2,4,14</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

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